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Preparation, characterization and adsorption properties of chitosan nanoparticles for eosin Y as a model anionic dye

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Abstract

The present study dealt with the adsorption of eosin Y, as a model anionic dye, from aqueous solution using chitosan nanoparticles prepared by the ionic gelation between chitosan and tripolyphosphate. The nanoparticles were characterized by atomic force microscopy (AFM), size and zeta potential analysis. A batch system was applied to study the adsorption of eosin Y from aqueous solution by chitosan nanoparticles. The results showed that the adsorption of eosin Y on chitosan nanoparticles was affected by contact time, eosin Y concentration, pH and temperature. Experimental data followed Langmuir isotherm model and the adsorption capacity was found to be 3.333 g/g. The adsorption process was endothermic in nature with an enthalpy change (ΔH) of 16.7 kJ/mol at 20–50 °C. The optimum pH value for eosin Y removal was found to be 2–6. The dye was desorbed from the chitosan nanoparticles by increasing the pH of the solution.

Keywords: Adsorption; Chitosan nanoparticles; Eosin Y; Atomic force microscopy (AFM); Zeta potential

1. Introduction

Dyes are widely used in textile industries. The wastewaters from these industries are important sources of water pollution. It has been estimated that worldwide annual production of dyes is around 7×10^5 t, 5–10% of which is discharged into water by the textile industries [1]. Dyes in wastewater undergo chemical changes, consume dissolved oxygen, and destroy aquatic life. Moreover, some dyes and their degradation products may be carcinogenic and/or toxic. So the wastewaters from the textile industries should be treated before their discharge into environment.

Many investigators have made great effort to study different techniques for removal of dyes in wastewater. Now, various types of technology are available such as chemical coagulation, cold point extraction [2–4], micellar enhanced ultrafiltration [2–4], nanofiltration [5], and adsorption on to kaolinite [6], activated agricultural solid waste [7], various types of activated carbon [8,9], and magnetic nanoparticles [10]. The activated carbon generally used for dye adsorption is very expensive.

Biosorption, which uses waste biomaterials as sorbents, is a newly developed technique [11,12] for the removal of harmful substances from water bodies, but suffers serious limitations in the case of anionic dyes as most of the biomaterials contain negatively charged cellulosic moieties, which lower adsorption due to coulombic repulsion.

Chitosan, a cationic polysaccharide, is easily obtained by partially deacetylation of chitin, which is the second most abundant biopolymer on earth only after cellulose and commonly found in the exoskeleton or cuticles of many invertebrates and in the cell wall of most fungi and some algae. Due to the unique polycationic nature, chitosan and its derivatives have been used for various applications in many different fields including biomedicine, food, agriculture, biotechnology and pharmaceutics [13]. Recent studies indicated that chitosan showed a higher capacity for adsorption of anionic dyes [14].

In the present study, chitosan nanoparticles were prepared with a narrow size distribution based on ionic gelation between positively charged chitosan and negatively charged tripolyphosphate. The nanoparticles were further used for the removal of

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eosin Y as a model anionic dye, to obtain information for treating effluents from the dye industry.

2. Materials and methods

2.1. Materials

Chitosan, from shrimp shell with a molecular weight of 150 kDa and deacetylation degree of 90%, was purchased from Yuhuan Ocean Biochemical Co. (Zhejiang Yuhuan, China). Tripolyphosphate (TPP) and eosin Y were obtained from Sigma Chemical Co. (USA). The water used throughout this work was the reagent-grade water produced by Milli-Q SP ultrapure-water system of Nihon Millipore Ltd., Tokyo. All other chemicals used were of analytical grade reagents commercially available and used without further purification.

2.2. Preparation of chitosan nanoparticles

Chitosan nanoparticles were prepared based on the ionic gelation of chitosan with TPP anions. Briefly, chitosan was dissolved in 1% (v/v) acetic acid to obtain a 0.2% (w/v) chitosan solution. TPP was dissolved in water to a concentration of 1%. Under magnetic stirring at room temperature, 1 ml of tripolyphosphate solution was added dropwise to 25 ml of chitosan solution. The mixture was stirred for a further 20 min followed by sonication. The resulting suspension was subsequently centrifuged at 12,000 × *g* for 10 min. The precipitate was suspended in water, centrifuged again and then freeze–dried. Then the freeze–dried chitosan nanoparticles were resuspended for characterization or directly used for adsorption experiments.

2.3. Characterization

Chitosan nanoparticles were visualized with atomic force microscopy (AFM, SPM-9500J3, Shimadzu CO., Japan) in the contact mode. Samples dissolved in water were placed onto freshly cleaved mica and dried in air at room temperature. AFM image was performed with a spring contact of $k = 0.03$ N/m using a nanoprobe cantilever made of silicon nitride (Si_3N_4).

Particle size distribution and zeta potential of chitosan nanoparticles were measured by Zetasizer Nano-ZS-90 (Malvern Instruments). The analysis was performed at a scattering angle of 90° at 25 °C. For zeta potential measurements, samples were diluted with 0.1 mM KCl and measured in the automatic mode.

2.4. Adsorption and desorption studies

The adsorption of eosin Y onto chitosan nanoparticles was carried out in a batch process by using aqueous solutions of eosin Y. The variable parameters were tested including contact time, initial dye concentration, pH of the medium and temperature. In each experiment except for the initial concentration experiment, 100 mg chitosan nanoparticles were added to 100 ml water solution of eosin Y with a known concentration. The pH value was adjusted by adding a few drops of dilute NaOH or HCl if necessary. The mixture, loaded in a 250 ml conical flask, was shaken at 100 rpm in the water bath of a thermostat at a particular temperature for different time intervals. Nanoparticles were removed by centrifuge at 12,000 × *g* for 10 min. The adsorption amounts of eosin Y were determined by the concentration change of eosin Y in solution after adsorption using spectrophotometric method at 517 nm (Pharmacia Biotech Ultrospec 2000).

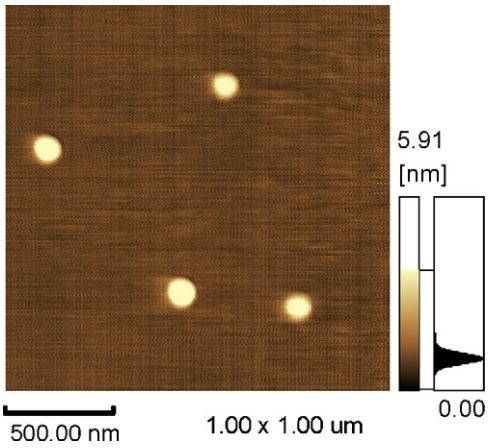

Fig. 1. AFM image of chitosan nanoparticles.

Desorption of eosin Y was performed by putting the removed nanoparticles into a clean 250 ml conical flask containing 100 ml water, and the pH was adjusted to 10.0, 11.0, and 12.0. The flasks were shaken at 100 rpm up to 20 h at 20 °C. The concentration of the eluted dye was determined at different time intervals by the same method described above.

3. Results and discussion

3.1. Characterization of chitosan nanoparticles

Chitosan solution changed from a clear solution to an opalescent suspension when TPP was added. This transformation indicated that ionic gelation occurred between chitosan and TPP, and nanoparticles formed. The chitosan nanoparticles prepared took on a white powder and could disperse in water, dilute acidic and alkali solutions without aggregation.

Fig. 1 showed the morphological characteristic of chitosan nanoparticles by AFM image. Chitosan nanoparticles prepared were regular spheres. The mean size, width of distribution and zeta potential are essential parameters for nanoparticles. Fig. 2 showed a typical size distribution profile of the nanoparticles with a mean diameter of 69.33 nm in a narrow size distribution

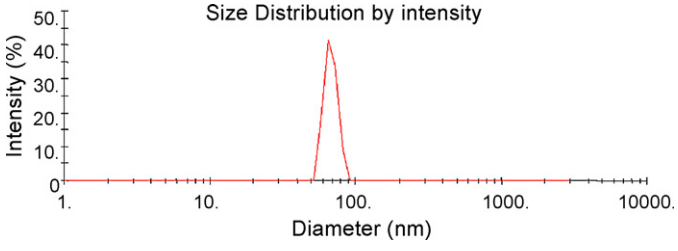

Fig. 2. Size distribution of chitosan nanoparticles.